
Dissolution of Cathode Materials in Lithium Secondary Batteries

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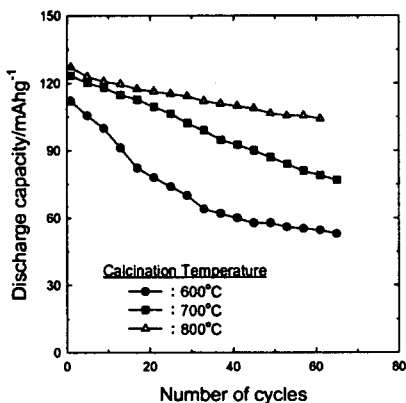
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Spinel LiMn_2O_4 & LiCoO_2

- Spinel LiMn_2O_4
 - Slow capacity fading at 4 V range
 - Inferior cyclability, particular at high temp. ($> 55^\circ\text{C}$)
 - Spinel dissolution.

- LiCoO_2
 - Increase of capacity fade at highly delithiated phase ($x > 0.5$, $\text{Li}_{1-x}\text{CoO}_2$)
 - Is it all related to structural instability?
 - Co dissolution and its suppression

Cyclability of Li/Li_xMn₂O₄ cells

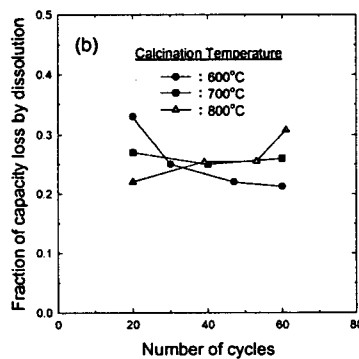
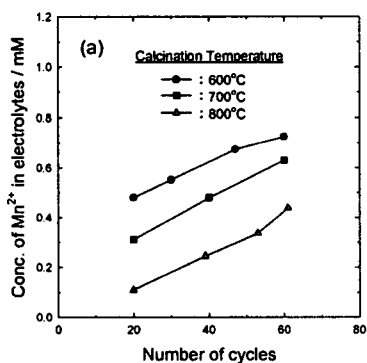


- Cathode composite
- Spinel : Vulcan XC-72 : binder
= 75 : 21 : 4 in wt ratio
- Constant current = 1 mAcm⁻²
- Cut-off voltage: 3.6 V - 4.3 V (vs. Li/Li⁺)

Calcination Temp.	Surface Area (m ² g ⁻¹)	Average Mn valence
600°C	21.20	3.61
700°C	11.89	3.55
800°C	3.64	3.53

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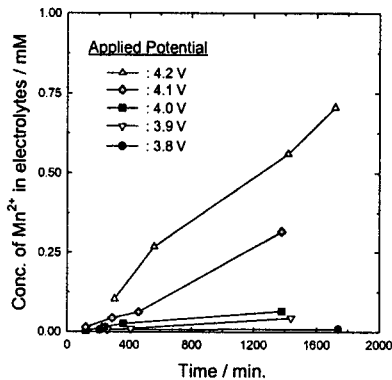
Spinel dissolution & Capacity Loss



- ✓ Mn²⁺ concentration steadily increases with repeated cycling in three cells.
- ✓ The *spinel's* surface area plays a key role in *spinel* dissolution.
- ✓ The material losses account for only 20 - 33 % of the overall capacity losses.

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Potential dependence of spinel dissolution



- Cathode composite

Spinel : Vulcan XC-72 : binder =
75 : 21 : 4 w/o

- 1 M LiClO₄ in PC/DME

- ✓ Spinel dissolution was notably high at the charged state (at > 4.1 V vs. Li/Li⁺)

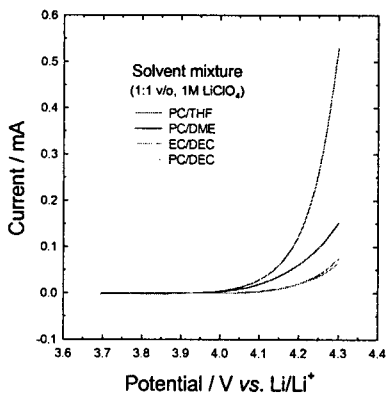
- ✓ Disproportionation reaction



This mechanism seems to be unlikely since the dissolution takes place at the end of a charging process.

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Electrochemical Oxidation of Solvent Molecules



- Carbon electrode

ketjenblack EC : binder = 86 : 14

- Scan rate = 1 mV/sec

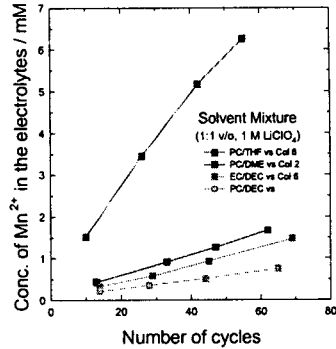
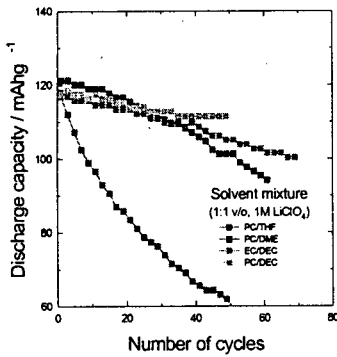
- ✓ Solvent Oxidation

THF > DME > DEC, PC

- ✓ Organic ethers are easily oxidized on carbon but carbonates are relatively inert.

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Cyclability & Spinel Dissolution



- composite cathode
600°C-calcined spinel : ketjenblack EC : binder
= 72 : 20 : 8 in wt ratio
- constant current : 1 mA/cm²
- cut-off voltage : 4.3 V - 3.6 V

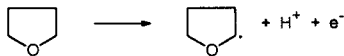
- ✓ In ether solvent, cyclability is poor.
- ✓ In carbonates, cyclability is better.
- ✓ Spinel dissolution is serious in ethers but it is minimal in carbonates

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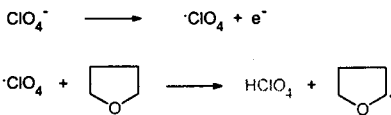
Active species in Spinel dissolution



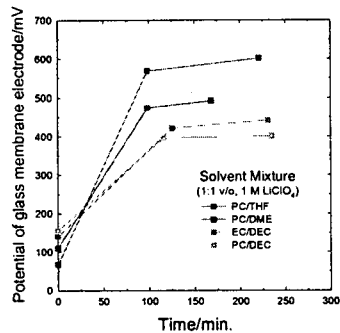
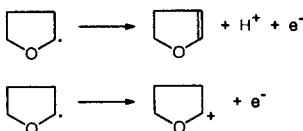
1) Direct oxidation of THF



2) Mediated oxidation via perchlorate radicals



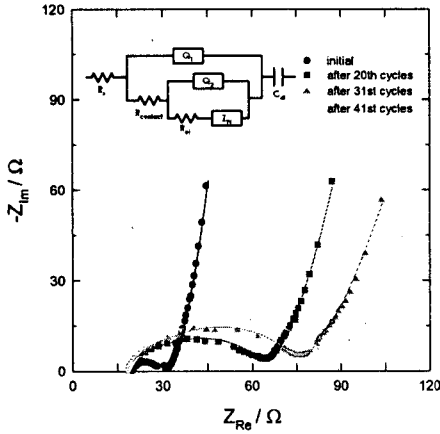
3) Further oxidation



- ✓ Acids play a key role in spinel dissolution.

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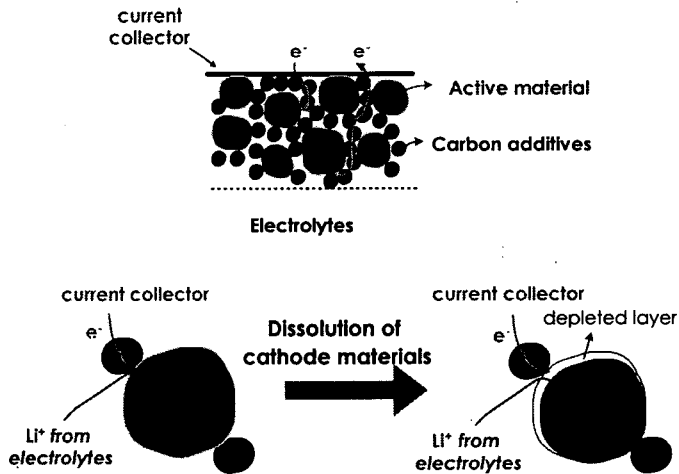
Ac Impedance Spectroscopy



- R_s : sol'n resistance
 - R_{contact} : contact resistance
 - R_{el} : electrode reaction resistance
 - C_{dl} : double-layer capacitance
 - Z_w : Warburg impedance
 - Q : CPE(constant phase element)
- spinel electrode : 600°C-calcined
 - composite cathode ;
spinel : carbon : binder = 75 : 21 : 4

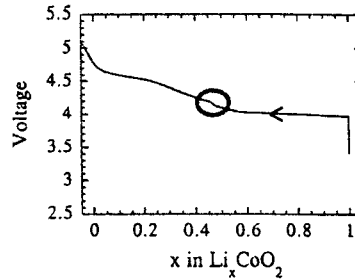
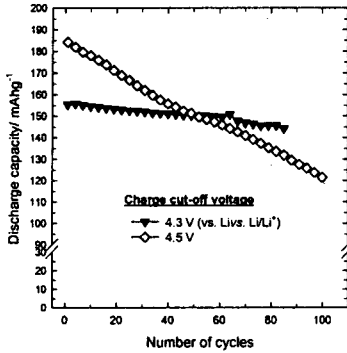
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Schematic illustration of polarization loss



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Electrochemical & structural characteristics of LiCoO_2



- Discharge cut-off voltage : 3.0 V vs. Li/Li^+
- Constant current = 0.6 mAcm^{-2} (0.5C)
- Electrolyte: 1M LiPF_6 in EC/DMC (1:2 v/o)

- Voltage plateau at 4.2-4.3 V
- Hexagonal to monoclinic phase transition
- Critical point of cyclability of LiCoO_2 cathode

Ref) T. Ohzuku *et al.*, *JES*, **141**, 2972(1994).
G. G. Amatucci *et al.*, *JES*, **143**, 1114(1996).

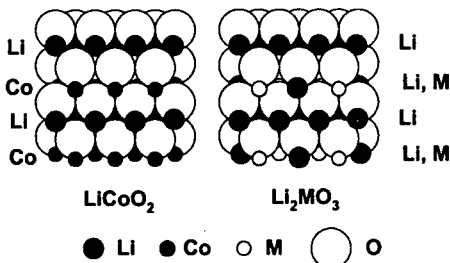
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Layered structured solid solutions of LiCoO_2 - Li_2MO_3



- $\text{LiM}_x\text{Co}_{1-x}\text{O}_2$ (M= Al, B, Mg, Fe, etc) → no improvement in cycle performances
- $\text{LiM}_x\text{Co}_{1-x}\text{O}_2$; LiMO_2 - LiCoO_2 solid solution

Crystal structure models of LiCoO_2 & Li_2MO_3

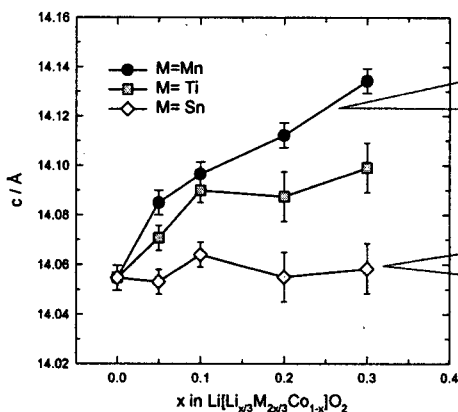


- ✓ Li_2MO_3 has a layered structure similar to LiCoO_2
 - LiCoO_2 : trigonal symmetry ($R\bar{3}m$)
 - Li_2MO_3 : monoclinic symmetry

- ✓ Solid solutions of LiCoO_2 - Li_2MO_3
 - $3\text{Co}^{3+} \rightarrow 2\text{M}^{4+} + \text{Li}^+$
 - $\text{Li}[\text{Li}_{x/3}\text{M}_{2x/3}\text{Co}_{1-x}]\text{O}_2$
 - M= Co (undoped), Ti, Mn, Ru, and Sn

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Variations of lattice constants of $\text{Li}[\text{Li}_{x/3}\text{M}_{2x/3}\text{Co}_{1-x}]\text{O}_2$



Continuous change of lattice constants means formation of solid solution of $\text{LiCoO}_2\text{-Li}_2\text{MnO}_3$.

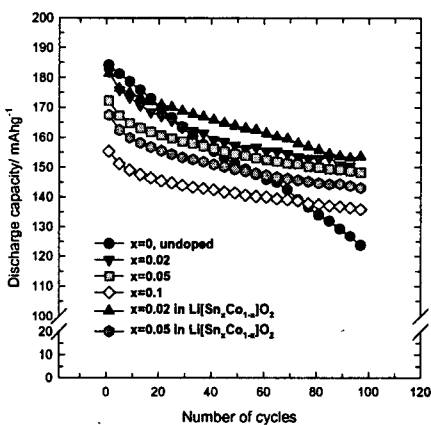
No change of lattice constants of LiCoO_2 means that the phases of $\text{LiCoO}_2\text{-Li}_2\text{SnO}_3$ exist separately (composite).

✓ Metal (M) ion size in $\text{Li}[\text{Li}_{x/3}\text{M}_{2x/3}\text{Co}_{1-x}]\text{O}_2$ is a critical factor for homogeneity of solid solution of $\text{LiCoO}_2\text{-Li}_2\text{MO}_3$

✓ Ionic radii of metal ion
 $\text{Co}^{3+}(\text{t}_2^g) = 0.545 \text{ \AA}$
 $\text{Mn}^{4+} = 0.53 \text{ \AA}$
 $\text{Ti}^{4+} = 0.605 \text{ \AA}$
 $\text{Ru}^{4+} = 0.62 \text{ \AA}$
 $\text{Sn}^{4+} = 0.69 \text{ \AA}$

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Cycling performances of $\text{Li}[\text{Li}_{x/3}\text{Sn}_{2x/3}\text{Co}_{1-x}]\text{O}_2$

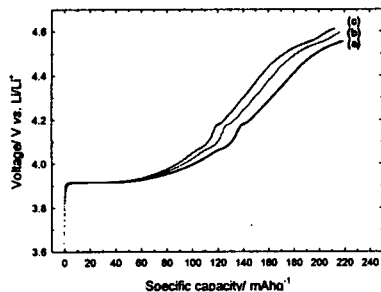


$\text{Li}[\text{Li}_{x/3}\text{Sn}_{2x/3}\text{Co}_{1-x}]\text{O}_2$	1 st discharge capacity (mAhg^{-1})	Capacity loss (%) ^a
Undoped	184	35
x=0.02	182	18
x=0.05	172	14
x=0.1	155	13
x=0.02 in $\text{Li}[\text{Sn}_x\text{Co}_{1-x}]\text{O}_2$	181	10
x=0.05 in $\text{Li}[\text{Sn}_x\text{Co}_{1-x}]\text{O}_2$	167	15

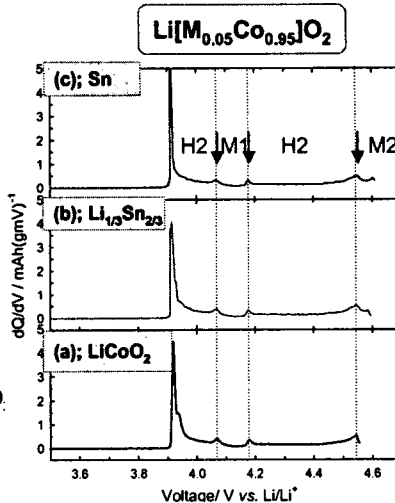
a: capacity losses after 100th cycle

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Voltage profiles & differential capacity plots



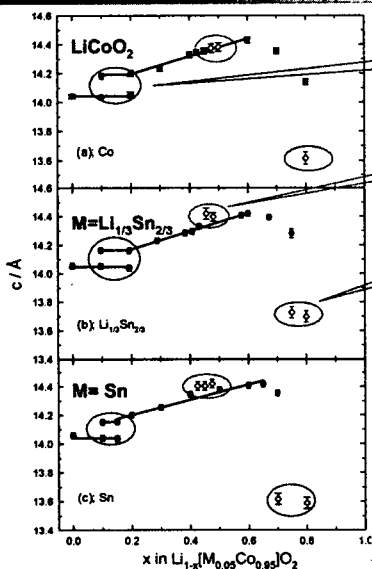
- Cells were charged to $x=0.8$ in $\text{Li}_{1-x}[\text{M}_{0.05}\text{Co}_{0.95}]\text{O}_2$
- Constant current = 0.04 mAcm^{-2} , 0.05 C rate



➤ Hexagonal to monoclinic phase transition still exist in all samples.

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Variation of c-axis lattice constants of as function of x in $\text{Li}_{1-x}[\text{M}_{0.05}\text{Co}_{0.95}]\text{O}_2$ during first charge



H1 & H2 2-phase coexistence

H2 → M1 phase transition

H2 → M2 phase transition

✓ Symbol H and M

➤ Hexagonal and monoclinic phase

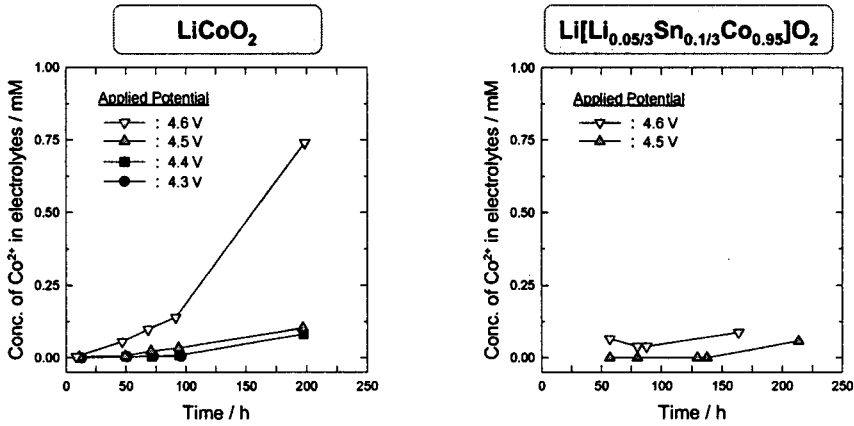
✓ Structural variation is very similar

✓ Variation of c-axis constants

- LiCoO_2 : $2.78\% (\pm 0.02)$
- $\text{M} = \text{Li}_{1/3}\text{Sn}_{2/3}$: $2.61\% (\pm 0.02)$
- $\text{M} = \text{Sn}$: $2.58\% (\pm 0.02)$

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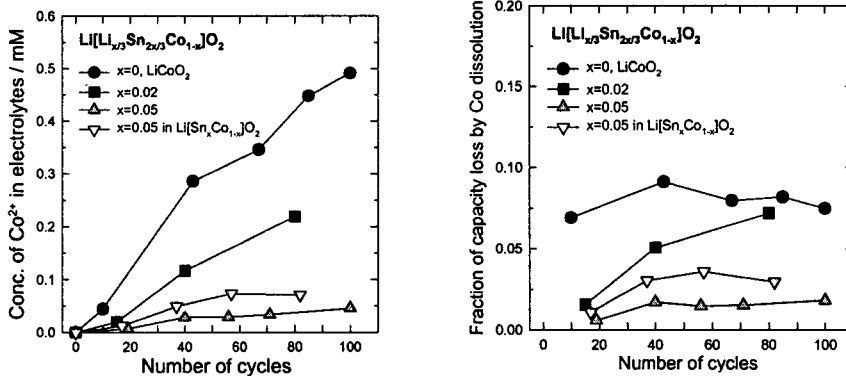
Conc. of Co^{2+} ions in the electrolytes as function of time and cathode potential



- Electrolyte: 1M LiPF₆ in EC/DMC (1:2 v/o)
- Cobalt dissolution was not appreciable at < 4.3 V, but steadily increased when the applied potential became more.

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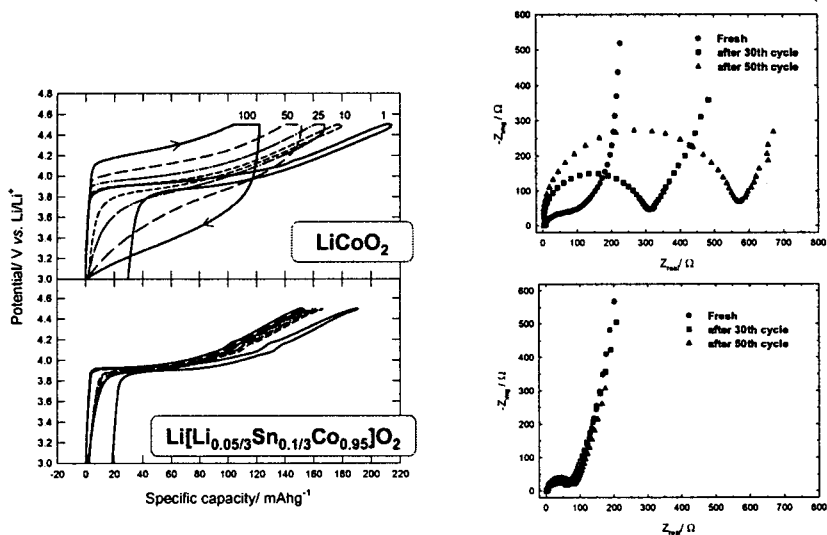
Conc. of Co^{2+} ions in the electrolyte with repeated cycling



- Cut-off voltage : 3.0 – 4.5V vs. Li/Li⁺
- Electrolyte: 1M LiPF₆ in EC/DMC (1:2 v/o)

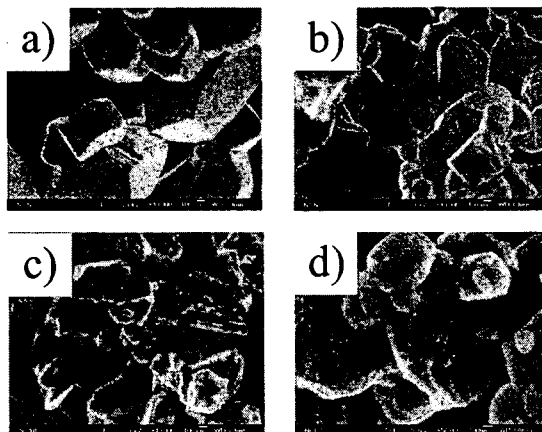
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Capacity fading via. polarization loss



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Surface morphology of LiCoO_2 & $\text{Li}[\text{Li}_{x/3}\text{Sn}_{2x/3}\text{Co}_{1-x}]\text{O}_2$



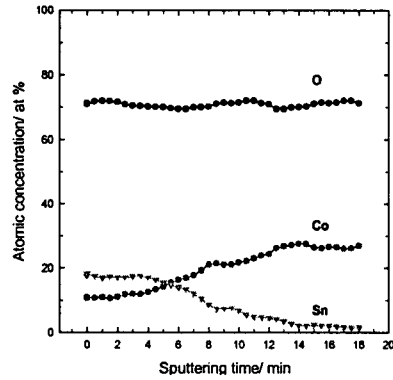
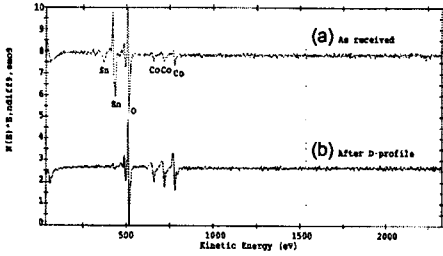
(a); LiCoO_2 , (b); $x=0.05$ in $\text{Li}[\text{Li}_{x/3}\text{Sn}_{2x/3}\text{Co}_{1-x}]\text{O}_2$, (c); $x=0.1$, (d); $x=0.2$

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Concentration profiles of Sn-doped LiCoO_2 particle by the Auger electron spectroscopy (AES)

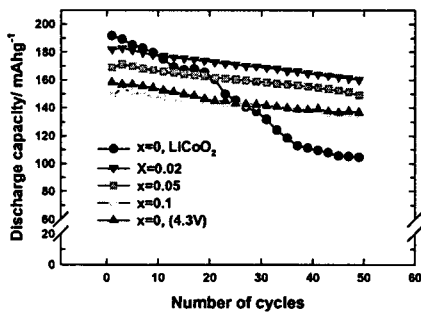


Auger traces of (a) before
(b) after sputtering



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Cycling performances of $\text{Li}[\text{Li}_{x/3}\text{Sn}_{2x/3}\text{Co}_{1-x}]\text{O}_2$ at 55°C



- Cut-off voltage : 3.0 V-4.5 V vs. Li/Li^+
- Constant current = 0.6 mAcm^{-2} , 0.5 C rate
- Electrolyte : 1M LiPF_6 in EC:DMC(1:2 v/o)

- Temp. \uparrow → Cathode dissolution \uparrow
- Sn-doped LiCoO_2 shows excellent capacity retention at 55 °C cycling condition, LiCoO_2 deteriorates fast.

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Conclusion



- Dissolution of cathode material is deeply related to capacity fading.
- Dissolution of cathode materials (spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xCoO_2) shows potential-dependent behaviors, which is related to electrolyte oxidation.
- It is likely that acids are produced as a result of the solvent oxidation and they play a key role in cathode dissolution.
- Solvent oxidation and spinel dissolution were severe in ethers (THF, DME), but minimal in carbonates (PC, EC, DEC).
- Dissolution of cathode material leads to capacity losses in two different ways; a material loss of the active component and a polarization loss resulting from an increment of cell resistances.
- Sn-doping makes minor effect on structural stability of LiCoO_2 , since Sn-doped LiCoO_2 also shows hexagonal to monoclinic phase transition.
- Sn doping into LiCoO_2 leads to formation of Sn-based compounds on the surface of LiCoO_2 and this layer plays a favorable role in suppressing the Co dissolution.

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